

Sorption and Diffusion of Water, Salt Water, and Concrete Pore Solution in Composite Matrices

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ABSTRACT: In recent years, the use of fiber-reinforced polymer composites in civil infrastructure has been promoted as a solution to the deterioration of bridges, buildings, and other structures composed of traditional materials, such as steel, concrete, and wood. Any application of a polymer composite in an outdoor environment invariably involves exposure to moisture. There is also potential for exposure to saline conditions in waterfront or offshore structures, and alkaline environments, as would be encountered by a reinforcing bar in a cementitious material. This study characterizes the sorption and transport of distilled water, salt solution, and a simulated concrete pore solution in free films of vinyl ester, isophthalic polyester (isopolyester) and epoxy resins, all commercially important materials for use in structural composites. Diffusion of all three liquids in each of the three materials was observed to follow a Fickian process. Mass loss was observed for the isopolyester in salt water and concrete pore solution at 60°C, suggesting hydrolysis that was accelerated by the high temperature exposure. Both the rate of uptake, as well as the equilibrium uptake, were greater at 60°C, compared with ambient conditions. Diffusion coefficients calculated from the mass uptake data revealed that, although the epoxy resin had the highest equilibrium uptake, it had the lowest diffusion coefficient. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 71: 483–492, 1999

Key words: building technology; composite materials; concrete pore solution; epoxy; diffusion; polyester; salt water; vinyl ester; water

INTRODUCTION

In recent years, the use of fiber-reinforced polymer (FRP) composites in civil infrastructure has been promoted as a solution to the deterioration of bridges, buildings, and other structures composed of traditional materials, such as steel, concrete, and wood. Applications for FRP materials are being found in structural components, reinforcing bars for concrete, prestressing tendons, and in the rehabilitation and retrofitting of steel

and concrete structures. Attractive features of FRP in such applications include its high strength-to-weight ratio, relative chemical inertness, and ease of installation, which should lead to savings in construction and maintenance costs for civil engineering structures.

Any application of a polymer composite in an outdoor environment inevitably involves exposure to moisture, either in the form of atmospheric vapor or rain. In addition, there is potential for exposure to saline environments, as in waterfront or offshore structures, and alkaline conditions, as would be encountered by a reinforcing bar in a cementitious material. Such environments may have a significant effect on the properties of the matrix resin and the composite.

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Changes in a polymer's glass transition temperature (T_g), viscoelastic response, and mechanical properties due to the influence of moisture are well-documented.¹⁻⁴ In a FRP composite, the polymer matrix may be plasticized and/or degraded, the interface could be weakened, and the fibers themselves could also be attacked by moisture. However, there is little information available in the literature on the sorption and transport behavior of water, salt water, and alkaline solutions in the composite as well as in the polymer matrix.

This study characterizes the diffusion behavior of distilled water, salt solution, and a simulated concrete pore solution in vinyl ester, isophthalic polyester (isopolyester), and epoxy resins—all commercially important materials for use in structural composites. Due to both the physical and chemical complexities of FRP it is instructive to first study diffusion and sorption behavior in the nonreinforced matrix component only. In this way, the response of the polymer matrix to liquid water, salt solution, and simulated concrete pore solution can be isolated from that of the fiber reinforcement and the fiber/matrix interphase region. Using gravimetric sorption techniques, the uptake behavior for the three polymers was studied in the three liquids at both ambient temperature (22°C) and at 60°C. Diffusion coefficients for the materials were calculated assuming linear Fickian behavior. An understanding of sorption and diffusion processes in these materials will contribute to knowledge of their performance in these liquid environments.

THEORETICAL CONSIDERATIONS

Diffusion in polymers occurs by the transport of a penetrant *via* random molecular motion.⁶ In glassy polymers, such as the type that are used in structural composites, diffusion behavior can be categorized as follows:

1. Case I or Fickian: rate of diffusion of the penetrant is much less than that of polymer segment mobility.
2. Case II: rate of diffusion is much greater than polymer segment mobility and is strongly dependent on swelling kinetics.
3. Anomalous or non-Fickian: rate of diffusion is comparable with polymer segment mobility.

Cases I and II represent two extremes of diffusion behavior, with anomalous diffusion falling in between (see ref. 5).

Fickian diffusion can be described using the one-dimensional form of Fick's Second Law of Diffusion:

$$\frac{\partial C}{\partial t} = -D \frac{\partial^2 C}{\partial x^2}, \quad (1)$$

which gives the change in concentration, C , as a function of the diffusion coefficient, D , and time, t , at any plane x in a material.⁶

The basis for most diffusion measurements in polymer/penetrant systems is measurement of total mass uptake by polymer as a function of time. Using appropriate boundary conditions for diffusion into a semi-infinite film exposed to an infinite bath of penetrant, the second law can be solved for the initial phase of uptake (short times) to obtain (see ref. 7):

$$\frac{M_t}{M_\infty} = \frac{4}{\ell} \sqrt{\frac{Dt}{\pi}} \quad (2)$$

where M_t is the relative mass uptake at a time t , M_∞ is the relative mass uptake at equilibrium, ℓ is film thickness, and D is diffusion coefficient.

Fickian diffusion behavior in a material can be confirmed if the following characteristics are observed⁸:

1. Both uptake and desorption plots of M_t/M_∞ *vs.* $t^{1/2}$ are initially linear.
2. This linear region extends to at least $M_t/M_\infty = 0.6$ for uptake.
3. Above the linear region, the curves are concave against the abscissa.
4. Uptake curves obtained by plotting M_t/M_∞ *vs.* $t^{1/2}/\ell$ (reduced sorption curves) should coincide regardless of film thickness.
5. Plots of uptake and desorption will only coincide when D does not vary with the concentration of the penetrant.

Many techniques are available for measuring penetrant uptake, including laser interferometry,⁹ microdielectrometry,¹⁰ Raman spectroscopy,¹¹ nuclear magnetic resonance imaging,¹² Fourier transform infrared (FTIR) spectroscopy,¹³ and the use of radiolabeled penetrants,¹⁴ among others. The most common technique, due to its simplicity and versatility, is gravimetric sorption. Gravi-

metric sorption involves exposing the specimen to a penetrant and monitoring the change in specimen mass with time. For liquid uptake experiments, a "blot-and-weigh" technique is often used. Mass uptake is referenced to the original mass of the specimen and is calculated by:

$$\text{Mass uptake} = \frac{M_t - M_o}{M_o} \quad (3)$$

where M_o is the original dry mass, and M_t is the mass of the wet specimen at time t .

EXPERIMENTAL APPROACH

Materials

Commercial vinyl ester, isopolyester, and epoxy resins were selected for this study. All three matrices are thermosetting materials suitable for fabricating FRP composites through pultrusion and resin transfer molding processes. Derakane 411-350PA* (Dow Chemical), a vinyl ester consisting of a bisphenol A epoxy backbone with terminal methacrylic acid functionality, was used. The isopolyester resin, Aropol 7240-T15 (Ashland Chemical), is produced from the reaction of isophthalic acid, glycols, and maleic anhydride. Both the vinyl ester and isopolyester resins are dissolved in styrene monomer, which also participates in free radical reactions with the resin to form the final cross-linked network. The epoxy resin of interest was EPON 828RS (Shell Chemical), a liquid difunctional bisphenol A/epichlorohydrin-derived resin with an average molecular weight of 378 g mol^{-1} . Jeffamine T403 (Huntsman Chemical), a curing agent based on polyethertriamine, was used to crosslink the epoxy.

Specimen Preparation

Vinyl ester specimens were prepared by hand-mixing the resin, 3% by mass of a methyl ethyl ketone peroxide catalyst containing 9% by mass active oxygen, and a small amount ($<0.5\%$ by mass) of a silicone defoaming agent until thor-

oughly blended. A similar procedure was followed for the isopolyester specimens, except only 2% by mass of the methyl ethyl ketone peroxide catalyst, and no silicone defoamer was used. Because both the vinyl ester and isopolyester resins were pre-promoted and preaccelerated, only the addition of the catalyst was necessary. To prevent oxygen inhibition of the free radical crosslinking reaction and also to minimize styrene evaporation, free films of vinyl ester and isopolyester were produced by molding between two sealed acrylic plates. Poly(ethylene terephthalate) films served as release sheets. Films were allowed to gel at room temperature (22°C), followed by a 2 h/ 150°C postcure in a circulating air oven. Final film thicknesses ranged from $230 \text{ }\mu\text{m}$ to $260 \text{ }\mu\text{m}$.

Epoxy specimens were prepared by mixing 100 parts by mass of EPON 828 with 42 parts by mass of Jeffamine T403. Before film formation, the mixture was degassed in a vacuum oven at 85 kPa. Free films having a dry thickness of $300 \text{ }\mu\text{m}$ were drawn down with a draw-down applicator on polished aluminum foil. Films were allowed to gel at room temperature (22°C) for 24 h, followed by a 2 h/ 125°C postcure in a circulating air oven.

Film Characterization

Prior to initiating the sorption experiments, the thermophysical and surface properties of the films were characterized. T_g s were measured using differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). DSC analysis was conducted in a DSC 2910 (TA Instruments); specimens were heated from 25°C to 180°C at a heating rate of 5°C min^{-1} . Three replicates were analyzed for each specimen.

Films were also studied *via* DMTA in a Rheometrics Solids Analyzer II, using a frequency of 10 Hz and tensile strain of 0.05%, over the range of 20°C to 180°C . Three replicates were analyzed for each specimen. These experiments also yielded dynamic moduli values above and below the T_g .

The surface-free energies of the films γ_s , along with their dispersive (nonpolar) γ_s^d and polar components γ_s^p , were determined by measuring the contact angles of water and methylene iodide ($5\text{-}\mu\text{l}$ drops). Static contact angles were measured on clean, dry films using a Rame-Hart contact angle goniometer. The left and right sides of at least three droplets were measured for each liquid on each polymer. The surface energy components were calculated by using the geometric mean method developed by Owens and Wendt.¹⁵

* Certain commercial equipment, instruments, or materials are identified in this article to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for this purpose.

Table I Surface Energies of Epoxy, Vinyl Ester, and Isopolyester Films (in mJ m^{-2})

Matrix	γ_s^d	γ_s^p	$\gamma_s (\gamma_s^d + \gamma_s^p)$	Polarity (γ_s^p/γ_s)
Epoxy	34.36	7.68	42.04	0.18
Vinyl ester	35.56	3.95	39.51	0.10
Isopolyester	34.73	13.34	48.07	0.28

Exposure Environments

Exposure environments of interest in this study were distilled water, salt solution (to simulate a marine or offshore environment), and an artificial concrete pore solution (to simulate the alkaline environment of a cured cementitious material, as would be encountered by reinforcing bars). The salt water solution was composed of 0.58 mol L^{-1} NaCl in distilled water and has an pH of ~ 6.7 . Concrete pore solution was formulated according to the procedure of Christensen and colleagues¹⁶ and is composed of 0.23 mol L^{-1} KOH, 0.14 mol L^{-1} NaOH, and $2.0 \times 10^{-3} \text{ mol L}^{-1}$ CaOH in distilled water. The pH of this solution is ~ 13.5 .

Sorption Studies

Polymer films having dimensions of $25 \text{ mm} \times 25 \text{ mm}$ were immersed in distilled water, salt water, and concrete pore solution in glass jars at ambient temperature (22°C), with each jar containing one specimen. Films were periodically removed from solution, rinsed with distilled water (in the case of salt water and concrete pore solutions), blotted dry, and weighed on a Mettler AT automatic balance. The rate of water and solution sorption was measured as the rate of change in mass with respect to the initial dry mass of the film, as described. Six films of each polymer were tested in each solution.

For uptake studies at 60°C , the procedure is similar to the one described previously, with the exception that the screw-top jars were placed in a

sand bath maintained at $60^\circ\text{C} \pm 2^\circ\text{C}$. Mass uptake was determined as previously described.

RESULTS AND DISCUSSION

Film Characterization

Table I presents values of the total surface-free energy γ_s , surface-free energy polar γ_s^p , and non-polar γ_s^d components, estimated using the geometric mean method. The observed values are fairly typical for polar polymers.¹⁷ The relative surface polarity of these materials is isopolyester $>$ epoxy $>$ vinyl ester. The polarity of the surface, given by γ_s^p/γ_s , also follows this ranking.

The thermophysical properties of the neat films are summarized in Table II. In the DMTA experiments, T_g was taken as the peak of the loss modulus (E'') curve. The T_g of vinyl ester and polyester are comparable, with the T_g of the epoxy material being somewhat lower. The average T_g s obtained from DSC are observed to be lower than those obtained by DMTA. This is not an unusual finding, because DMTA and DSC measurements are conducted on different time scales or frequencies. Generally, DMTA measurements will yield higher T_g values than those obtained by dilatometry or by thermodynamic methods such as DSC. The dynamic moduli obtained for all three matrices at 20°C are roughly equivalent. However, in the rubbery plateau region ($T > 150^\circ\text{C}$), the epoxy is much more compliant than either the vinyl ester or polyester.

Mass Uptake Experiments

Before discussing the sorption and transport behavior of liquids in these polymer matrices, we wish to clarify the use of the terms *absorption* and *adsorption*. Absorption and adsorption are two completely different phenomena. Absorption is a capillary uptake by existing pores in a material, such as in the case of water taken up by concrete.

Table II Thermophysical Properties of Epoxy, Vinyl Ester, and Isopolyester Films

Matrix	T_g : DSC ($^\circ\text{C}$)	T_g : DMTA ($^\circ\text{C}$)	Dynamic Modulus $T = 25^\circ\text{C}$ (Pa)	Dynamic Modulus $T = 150^\circ\text{C}$ (Pa)
Epoxy	80.14	87.54	2.27×10^9	5.11×10^6
Vinyl ester	100.96	111.45	2.73×10^9	1.77×10^7
Isopolyester	105.01	117.52	2.77×10^9	2.00×10^9

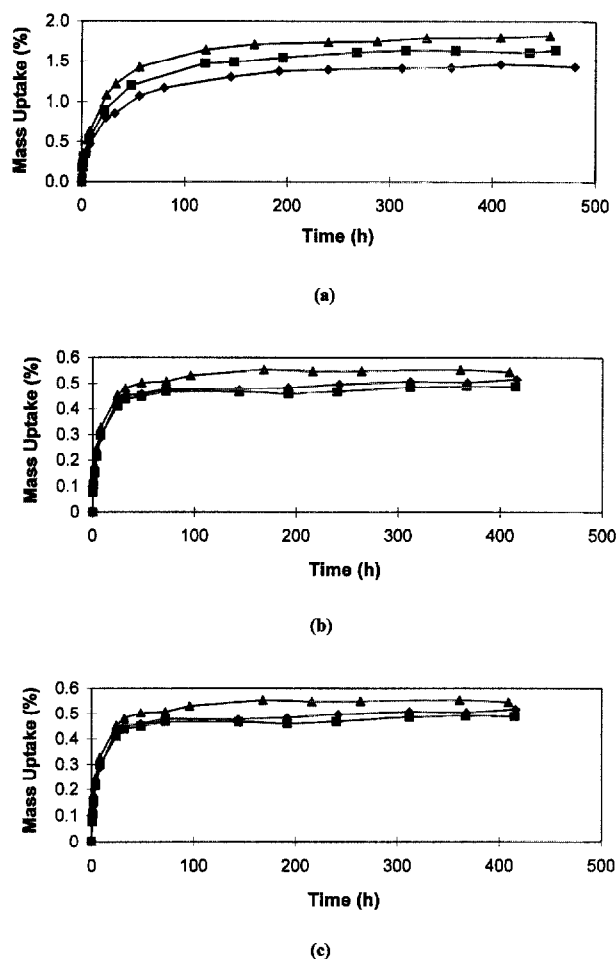


Figure 1 Mass uptake curves for (a) epoxy, (b) vinyl ester, and (c) isopolyester in water (◆), salt solution (▲), and concrete pore solution (■) at 22°C.

This process does not plasticize the matrix and generates little heat or swelling.

Adsorption, on the other hand, is the process by which a solution is formed. This process generates heat (heat of solution) and results in swelling, as observed when a polymer is immersed in an organic solvent. For a polymer free of voids or pores, the uptake of water is mainly an adsorption process. If a polymer contains pores, air bubbles, or other such defects, both absorption and adsorption take place. In such a case, the term *uptake* or *sorption* should be used.

As shown in Figure 1, mass uptake plots for epoxy, vinyl ester, and isopolyester at 22°C show an initial linear region, followed by a region concave to the abscissa. As will be discussed later, plots of M_t/M_∞ vs. $t^{1/2}/\ell$ also show a linear region up to or beyond $M_t/M_\infty = 0.6$, thus allowing this behavior to be characterized as Fickian. Uptake was rapid in the first 10 h, but slowed down between 10 h and 100 h, after which equilibrium was reached.

Equilibrium mass uptake for epoxy was greater than that of either vinyl ester or isopolyester, as summarized in Table III. The chemical structure and morphology of a polymer are known to affect uptake; in particular, a high concentration of polar functional groups can promote increased sorption of polar penetrants.¹⁸ The epoxy resin has significant concentration of hydrophilic hydroxyl groups located along the backbone. Vinyl ester and isopolyester contain the less polar ester moieties and hence are less hydrophilic. In general, the more polar groups present in the

Table III Equilibrium Mass Uptake for Epoxy, Vinyl Ester, and Isopolyester Films (Uncertainties Are Equivalent to One Standard Deviation)

Matrix	Sorbent	Equilibrium Mass Uptake (mass %)	
		22°C	60°C
Epoxy	Distilled water	1.42 ± 0.03	2.00 ± 0.10
	Salt solution	1.79 ± 0.04	1.93 ± 0.08
	Pore solution	1.64 ± 0.04	1.88 ± 0.06
Vinyl ester	Distilled water	0.52 ± 0.01	0.62 ± 0.05
	Salt solution	0.55 ± 0.01	0.69 ± 0.04
	Pore solution	0.49 ± 0.04	0.64 ± 0.03
Isopolyester	Distilled water	0.56 ± 0.02	0.5 ± 0.08
	Salt solution	0.55 ± 0.03	0.45 ± 0.10 ^a
	Pore solution	0.50 ± 0.04	0.49 ± 0.05 ^a

^a Maximum mass uptake before mass loss.

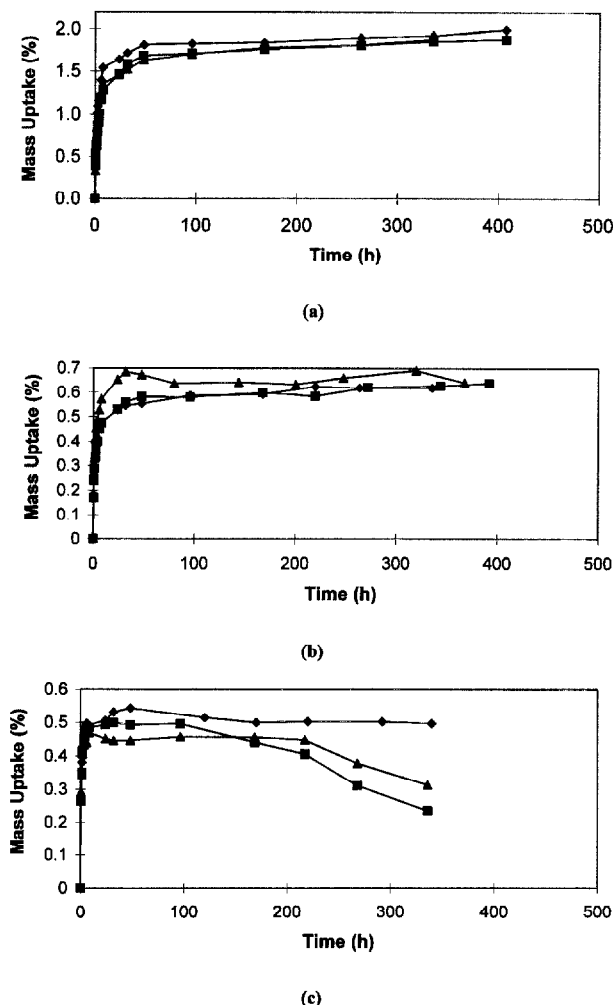


Figure 2 Mass uptake curves for (a) epoxy, (b) vinyl ester, and (c) isopolyester in water (◆), salt solution (▲), and concrete pore solution (■) at 60°C.

polymer matrix, the higher will be its sorptive affinity toward water.¹⁹

Figure 2 presents mass uptake as a function of time for the three polymers at 60°C. The rate of approach to equilibrium is clearly more rapid at 60°C relative to that at 22°C, which is an expected result. In addition to the increased rate of uptake, the equilibrium mass uptake at 60°C, shown in Table III, for the epoxy and vinyl ester also appears to be slightly higher than that at 22°C, even when the standard deviation of the data is taken into account. This could be due to the fact that sorption at room temperature may not have reached equilibrium in the same time frame as sorption at 60°C. Also, evidence exists to suggest that actual moisture equilibrium in epoxies may take years to achieve.²⁰ Other studies have re-

ported that hygrothermal aging of polymers at elevated temperature may create damage in the form of crazing, microcracking, and other types of morphological changes, thus allowing additional sorption to occur.²¹ This observation of higher equilibrium uptake at elevated temperature would need to be accounted for in any aging test using temperature as the accelerating factor; that is, not only is the rate of diffusion accelerated, but the equilibrium uptake is also increased.

The equilibrium uptake (Table III) does not seem to be correlated with the polymer polarity (Table I). This observation could be explained by the fact that the polarity obtained from the contact-angle measurement is associated with the surface and near-surface regions of the films, and not the bulk polymer. Furthermore, water uptake in a polymer is also affected by its microstructure and crosslink density, in addition to bulk polarity.

Unusual behavior is demonstrated by the isopolyester matrix in salt and pore solutions. As given in Table III, equilibrium mass uptake for the 60°C isopolyester exposures in salt and pore solutions is lower than that observed at 22°C. In addition, Figure 2(c) shows a decrease in mass uptake as a function of time beginning at 100 h for samples immersed in pore solution, and at 200 h for samples in salt solution. This mass loss can be explained by ester hydrolysis and subsequent leaching of low molecular weight, hydrolyzed fragments.^{22,23} Mass uptake curves of this type have also been reported for epoxy²⁴ and vinyl ester.²⁵ In all cases, the anomalous uptake behavior was attributed to irreversible degradation and/or leaching of unbound material, such as residual monomer.

To verify this hypothesis, infrared analysis was conducted on pore solution in which isopolyester films had been immersed at 60°C for 1 month. This pore solution was filtered, rinsed, dried on a zinc selenide crystal, and analyzed *via* attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR). The spectrum displayed in Figure 3 shows a double peak centered at 1557 cm^{-1} and a single peak at 1420 cm^{-1} assigned to carboxylate (COO^-) anion stretching. The peak at 1019 cm^{-1} is tentatively assigned to O—H bending. Two small shoulders on the main O—H stretching peak at 3334 cm^{-1} fall in the region of 2800 cm^{-1} and could be evidence of C—H stretching.

This spectrum suggests the presence of organic fragments and carboxylic acid salts in the pore

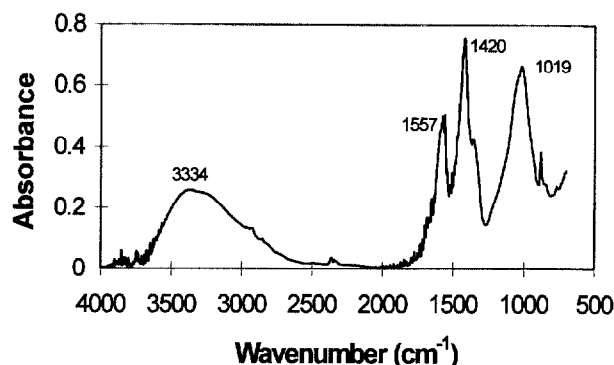


Figure 3 FTIR spectrum of concrete pore solution after immersion of isopolyester at 60°C.

solution after immersion of isopolyester at elevated temperature. The observations of these materials in the pore solution after immersion of isopolyester may be explained by the alkaline hydrolysis of ester groups. It is known that carboxyl groups result from the base-catalyzed hydrolysis of ester linkages



and can further react with hydroxides, such as KOH or NaOH, to yield carboxylate anion, COO^- via the following reaction:



The FTIR spectrum shown in Figure 3, which shows evidence of both carboxylic acid and carboxylate anion, supports this postulate.

As seen in Figure 2(c), isopolyester underwent mass loss not only in an alkaline environment, but also in salt solution. Hydrolytic degradation in neutral NaCl probably occurred via the following reactions:



Hydrolysis of esters in neutral medium generally occurs extremely slowly; however, the presence of sodium cations and subsequent formation of the carboxylate salt shown in ref. 5 accelerates hydrolytic degradation in the salt solution.²⁶ The obser-

vation that no mass loss occurred for the polyester specimens in distilled water at either temperature supports this hypothesis. The more rapid degradation of the polyester specimens in concrete pore solution, compared with polyester in the salt solution, is explained by the fact that OH^- present in the concrete pore solution is a much stronger nucleophile than water in the neutral salt solution. Thus, nucleophilic substitution reaction at the carbonyl carbon of the ester group is more rapid with OH^- than with water, leading to more rapid degradation.

Vinyl ester is generally considered to be more stable to hydrolysis than polyester, due to the fact that the ester linkages in vinyl ester are terminal and are shielded by methyl functional groups. Evidence for this postulate is provided by the observation that no mass loss occurred in the vinyl ester specimens in any environment, even at elevated temperature. In contrast, ester groups in the polyester specimens are distributed throughout the main chain and are more available and hence vulnerable to hydrolytic attack.

For the vinyl ester and polyester specimens, there is no significant difference in the amount of uptake between distilled water, salt solution, or concrete pore solution. This observation suggests that the main component sorbed from both salt solution and concrete pore solution is water. However, for the epoxy specimens, notable differences were observed in equilibrium uptake between the distilled water, salt solution, and pore solutions at 22°C. The reason for these differences is not yet known. Energy dispersive X-ray analysis of the specimens after sorption experiments showed no evidence of sodium, potassium, calcium, or chloride penetration into the bulk polymers.

Determination of Solubilities

Equilibrium mass uptake in the films can also be expressed in terms of solubility (i.e., the mass of sorbed penetrant per unit volume of film). Because solubility is basic to the understanding of the transport processes in materials, the determination of the solubilities of the three solutions in the three matrices studied should provide useful data for polymer and composite materials used in civil engineering applications. Solubilities of the three penetrants in the resins (listed in Table IV), was calculated by multiplying the equilibrium mass uptake by film density.²⁷ Density of the films was determined by the water displacement method and was calculated using the Archimedeian equation:

Table IV Solubility Values for Epoxy, Vinyl Ester, and Isopolyester Films

Matrix	Density (g cm ⁻³)	Sorbent	Solubility (mg cm ⁻³)	
			22°C	60°C
Epoxy	1.140	Distilled water	16.22	22.79
		Salt solution	20.45	22.03
		Pore solution	18.66	21.49
Vinyl ester	1.136	Distilled water	5.87	7.09
		Salt solution	6.30	7.85
		Pore solution	5.56	7.25
Isopolyester	1.156	Distilled water	6.46	6.63
		Salt solution	6.40	5.73
		Pore solution	5.80	6.11

$$\rho_2 = \frac{A}{P} \cdot \rho_o \quad (9)$$

where ρ_2 is the film density, A is the dry weight of the film, P is the buoyancy of the film, and ρ_o is the density of water. The densities of the films were similar; therefore, the solubility values parallel the values obtained for equilibrium uptake.

Determination of Diffusion Coefficients

Figures 4 and 5 display representative Fickian diffusion plots of M_t/M_∞ vs. $t^{1/2}/L^{-1}$ (reduced sorption curves) for epoxy resin in distilled water, salt solution, and pore solution at 22°C and 60°C, respectively. As noted earlier, the linear initial curve indicates that diffusion followed a Fickian process. Fickian diffusion plots for vinyl ester and isopolyester at 22°C and 60°C are similar in appearance and are not shown here. Due to the degradation exhibited by the isopolyester matrix in concrete pore and salt solutions at 60°C, this data was not plotted and could not be used to calculate diffusion coefficients. The lack of uptake equilibrium makes any estimate of D questionable, because penetrant uptake and desorption of degraded material may be occurring simultaneously.⁸

Diffusion coefficients for the three matrices are given in Table V. These were calculated as previously described using the data in the initial linear uptake region. At 60°C, isopolyester showed the highest diffusion coefficient, followed by vinyl ester, and then epoxy. At ambient temperature, lit-

tle difference existed between the isopolyester and vinyl ester values. These values are in good agreement with diffusion coefficients reported for liquid water in other polar polymers such as clear epoxy coatings (1.0×10^{-8} cm² s⁻¹),¹³ alkyd-melamine (1.5×10^{-8} cm² s⁻¹),²⁸ and nylon (1.0×10^{-9} cm² s⁻¹).²⁹ Ranking of the materials in terms of equilibrium uptake or solubility does not match the order of diffusion coefficients. The highest diffusion coefficients are observed for isopolyester, whereas the highest solubility is exhibited by epoxy. Although the epoxy resin exhibited the highest equilibrium uptake or solubility

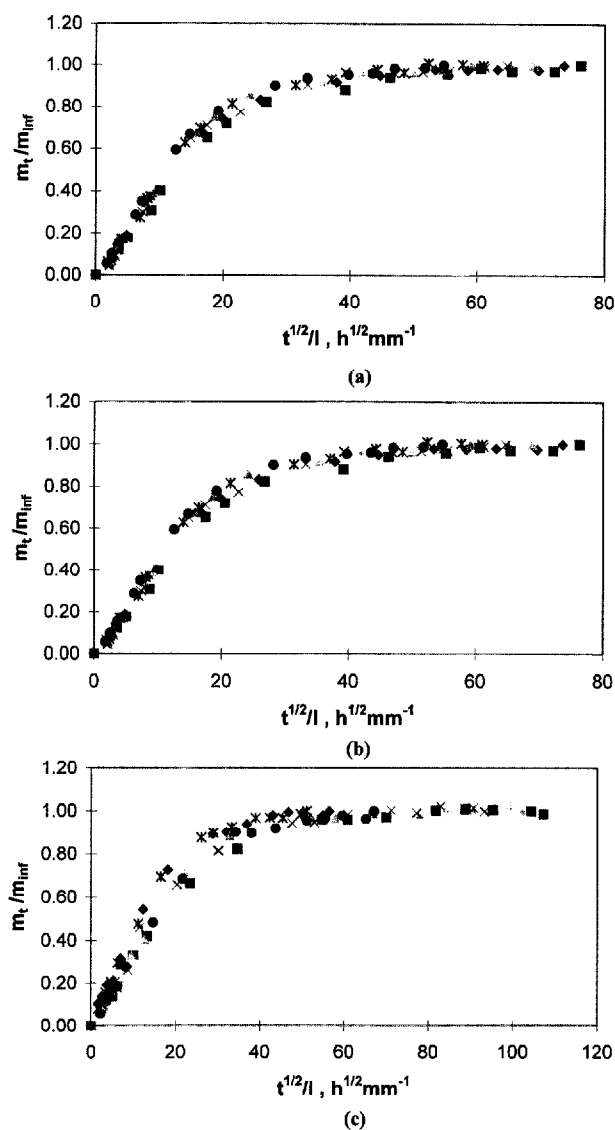


Figure 4 Fickian diffusion curves for epoxy in (a) water, (b) salt solution, and (c) concrete pore solution at 22°C.

of all three resins, it has the lowest diffusion coefficients. This is understandable since diffusion is a function of permeability and solubility. Obviously, the permeability of the epoxy is lower than that of isopolyester and vinyl ester.

As expected, diffusion coefficients calculated for the 60°C data are higher than those at 22°C. Diffusion coefficients were not calculated for isopolyester in pore solution and salt solution at 60°C, due to the weight loss and apparent degradation that occurred. Both diffusion coefficients and solubility data can be used to provide information on the permeability of these liquids in the polymer matrix.

Table V Fickian Diffusion Coefficients for Epoxy, Vinyl Ester, and Isopolyester Films

Matrix	Sorbent	Diffusion Coefficient, D ($\times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$)	
		22°C	60°C
Epoxy	Distilled water	0.53	13.6
	Salt solution	1.04	8.54
	Pore solution	0.67	9.82
Vinyl ester	Distilled water	6.88	19.0
	Salt solution	8.75	24.5
	Pore solution	8.72	24.3
Isopolyester	Distilled water	8.93	41.9
	Salt solution	11.7	—
	Pore solution	8.89	—

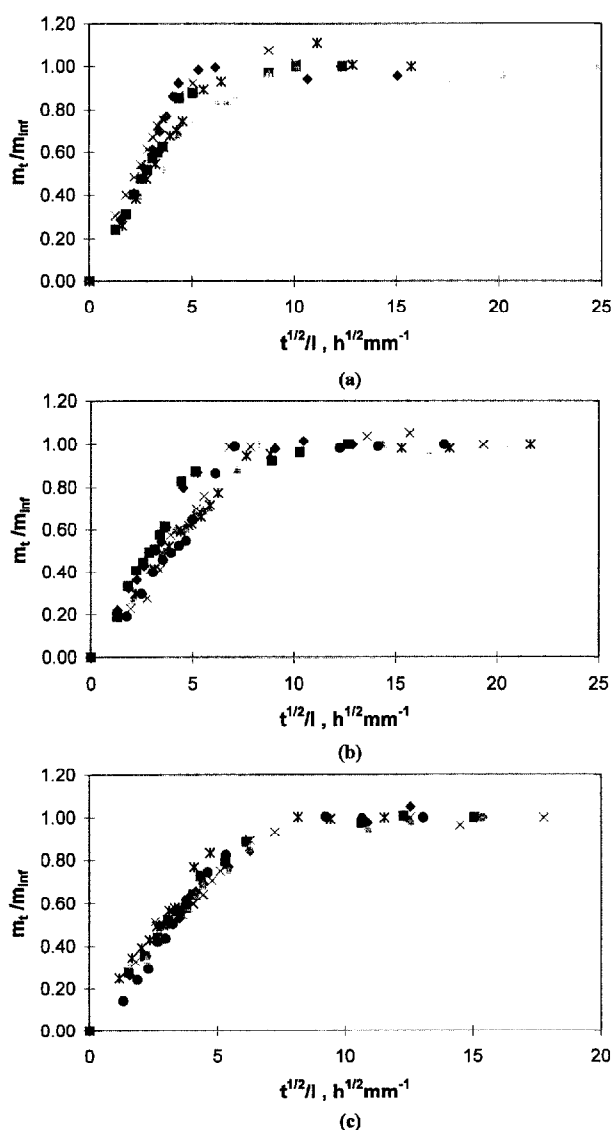


Figure 5 Fickian diffusion curves for epoxy in (a) water, (b) salt solution, and (c) concrete pore solution at 60°C.

SUMMARY AND CONCLUSIONS

The sorption and transport behavior of distilled water, salt solution, and concrete pore solution in epoxy, vinyl ester, and isopolyester matrices were studied. Diffusion of all three liquids in the three materials was observed to follow a Fickian process. Mass loss was observed for the isopolyester in concrete pore solution at 60°C, consistent with the fact that both alkaline conditions and elevated temperature promote hydrolysis of ester groups. Mass loss in isopolyester in the 60°C salt solution is driven by the presence of sodium cations and the formation of carboxylate salts. For the epoxy and vinyl ester matrices, both the rate of uptake as well as the equilibrium uptake was $>60^\circ\text{C}$, compared with ambient conditions. Diffusion coefficients calculated from the mass uptake data revealed that, although the epoxy resin had the highest equilibrium uptake of the three matrices studied, it had the lowest diffusion coefficient.

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REFERENCES

1. Thomason, J. L. *Composites* 1995, 26, 477.

2. Shen, C.-H.; Springer, G. S. in *Environmental Effects on Composite Materials*, Springer, G. S., Ed., Technomic Publishing Company, Lancaster, 1981, p. 79.
3. Collings, T. A.; Harvey, R. J.; Dalziel, A. W. *Composites* 1993, 24, 625.
4. Selzer, R.; Friedrich, K. *J Mater Sci* 1995, 30, 334.
5. Marom, G. in *Polymer Permeability*, Comyn J., Ed., Elsevier: New York, 1975, p. 341.
6. Crank, J.; Park, G. S. *Diffusion in Polymers*, Academic Press: New York, 1968.
7. Crank, J. *Mathematics of Diffusion*, 2nd ed., Oxford University Press: New York, 1975.
8. Comyn, J. in *Durability of Structural Adhesives*, Kinloch, A. J., Ed., Applied Science Publishers: New York, 1983, p. 84.
9. Saenger, K. L.; Tong, H. M. *Polym Eng Sci* 1991, 31, 432.
10. Day, D. R. in *New Characterization Techniques for Thin Polymer Films*, Tong, H. M.; Nguyen, L. T., Eds., John Wiley and Sons: New York, 1990, p. 1.
11. Schlotter, N. E. *J Phys Chem* 1990, 94, 1692.
12. Grinsted, R. A.; Koenig, J. L. *Macromolecules* 1992, 25, 1229.
13. Nguyen, T.; Bentz, D.; Byrd, E. *J Coat Technol* 1995, 67, 37.
14. Marshall, J. M.; Marshall, G. P.; Pinzelli, R. F. *Proceedings of the 37th Annual Conference, Reinforced Plastics/Composites Institute, The Society of the Plastics Industry, Inc.*, 1982, p. 9.C/1.
15. Owens, D. K.; Wendt, K. C. *J Appl Polym Sci* 1969, 13, 1741.
16. Christensen, B. J.; Mason, T. O.; Jennings, H. M. *J Am Ceram Soc* 1992, 75, 939.
17. Hata, T.; Kitazaki, Y.; Saito, T. *J Adhesion* 1987, 21, 177.
18. Apicella, A.; Nicolais, L.; Carfagna, C. in *The Role of the Polymeric Matrix in the Processing and Structural Properties of Composite Materials*, Seferis, J. C.; Nicolais, L., Eds., Plenum Press: New York, 1981, p. 215.
19. Barrie, J. A. in *Diffusion in Polymers*, Crank, J.; Park, G. S., Eds., Academic Press: New York, 1968, p. 259.
20. Lee, H. *Materials Research & Standards*, November 1963, 910.
21. Apicella, A.; Nicolais, L. *Ind Eng Chem Prod Res Dev* 1981, 20, 138.
22. Morii, T.; Tanimoto, T.; Hainada, H.; Maekawa, Z.; Hirano, T.; Kiyosumi, K. *Comp Sci Technol* 1993, 49, 209.
23. Apicella, A.; Migliaresi, C.; Nicolais, L.; Iaccarino, L.; Roccotelli, S. *Composites* 1983, 14, 387.
24. Bonniau, P.; Bunsell, A. R. in *Environmental Effects on Composite Materials*, Vol. 2, Springer, G. S., Ed., Technomic Publishing Company, Lancaster, 1984, p. 209.
25. Hojo, H.; Tsuda, K.; Ogasawara, K.; Mishima, K. *Progr Sci Eng Comp* 1982, 2, 1017.
26. Nguyen, T.; Hubbard, J. B.; Pommersheim, J. M. *J Coat Technol* 1996, 68, 45.
27. Moylan, C. R.; Best, M. E.; Ree, M. *J Polym Sci Part B Polym Phys* 1991, 29, 8.
28. Yaseen, M.; Funke, W. *J Oil Colour Chemists Assoc* 1978, 61, 284.
29. Asada, T.; Onogi, S. *J Colloid Sci* 1963, 18, 784.